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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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EVERT VAN DER HEIDE ET AL	)	
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Serial No. 10/802,630	)	Examiner:
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PROCESS FOR THE PREPARATION OF	)	April 8, 2004
PROPYLENE GLYCOL	)	
	)	

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**CLAIM TO PRIORITY**

Applicants reaffirm the claim for the benefit of filing date of the following foreign patent applications referred to in Applicants' Declaration:

EPC Application Serial No. 03251986.0 - filed March 28, 2003

Respectfully submitted,

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Enclosure



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The attached documents  
are exact copies of the  
European patent application  
described on the following  
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Les documents fixés à  
cette attestation sont  
conformes à la version  
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**Patentanmeldung Nr.    Patent application No.    Demande de brevet n°**

03251986.0

Der Präsident des Europäischen Patentamts;  
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets  
p.o.

**R C van Dijk**





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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:  
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.  
If no title is shown please refer to the description.  
Si aucun titre n'est indiqué se référer à la description.)

Process for the preparation of alkylene glycol

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PROCESS FOR THE PREPARATION OF ALKYLENE GLYCOL

The present invention relates to a process for the preparation of alkylene glycol from alkylene oxide.

Background of the invention

It is well known to contact alkylene oxide with carbon dioxide in the presence of a suitable catalyst to obtain a cyclic alkylene carbonate. Such process has been described for example in EP-A-119840. Further, it is known that the cyclic alkylene carbonate can be converted further. A conventional further process comprises hydrolysis of the cyclic alkylene carbonate to produce a diol as is described in US-A-5,847,189.

Summary of the invention

We have now found that the preparation of alkylene glycol from alkylene oxide can be improved in a simple and efficient way. It was found that the presence of a substantial amount of alkylene oxide is advantageous during the hydrolysis of the cyclic carbonate. Alkylene oxide present during the hydrolysis of cyclic carbonate, was converted with water into alkylene glycol without formation of substantial amounts of by-products. This is surprising as the reaction of propylene oxide with water in the presence of catalyst to obtain 1,2-propanediol is known to give substantial amounts of dipropylene glycol if no further compounds are present.

An advantage of the conversion of propylene oxide with water into 1,2-propanediol in the presence of cyclic carbonate is that this reaction generates heat which can be used in the endothermic conversion of the cyclic

carbonate. Therefore, less cooling is needed during the conversion of alkylene oxide while less heating can be carried out during the conversion of the cyclic carbonate.

5       A further advantage of the presence of alkylene oxide in the hydrolysis of the cyclic carbonate is the fact that it is not required to remove all alkylene oxide from the cyclic carbonate before further conversion such as by full conversion of the alkylene oxide.

10       The present invention relates to a process for the preparation of alkylene glycol from alkylene oxide, which process comprises (a) contacting alkylene oxide with carbon dioxide in the presence of catalyst to obtain a first reaction mixture containing cyclic carbonate, and  
15       (b) contacting at least part of the first reaction mixture with water in the presence of catalyst to obtain a second reaction mixture containing alkylene glycol and carbon dioxide, in which process a substantial amount of alkylene oxide is present in step (b).

20       Detailed description of the invention

      In process step (a) of the present invention, the alkylene oxide is contacted with carbon dioxide in the presence of catalyst. Several catalysts are known to be suitable for such process. Preferably, the catalyst is a  
25       homogeneous catalyst, more specifically a phosphorus containing homogeneous catalyst. Well known phosphorus containing compounds which are suitable catalysts are phosphine compounds and phosphonium compounds. The catalyst preferably is a homogeneous phosphonium  
30       catalyst, more specifically a phosphonium halide catalyst. It was found especially advantageous to employ a tetraalkylphosphonium halide catalyst, more specifically a tributyl-methyl phosphonium iodide.



The catalyst can be either added as such or can be formed in-situ.

The alkylene oxide for use in the present invention can in principle be any alkylene oxide known to be suitable. Preferably, the alkylene oxide contains of from 2 to 5 carbon atoms. More preferably, the alkylene oxide employed is ethylene oxide and/or propylene oxide. Most preferably, the alkylene oxide is propylene oxide. The use of propylene oxide starting compound in the present invention, makes that propylene carbonate is formed in step (a) which leads to the manufacture of 1,2-propanediol or monopropylene glycol in step (b). In such process, the alkylene glycol is 1,2-propanediol and the alkylene oxide is propylene oxide.

The carbon dioxide can be either pure carbon dioxide or carbon dioxide containing further compounds. Carbon dioxide which is especially suitable for use in the present invention, is carbon dioxide which has been separated off in subsequent steps of the present process. Carbon dioxide can either be separated off directly after the alkylene oxide has reacted with carbon dioxide or at a later stage.

Carbon dioxide is produced in the reaction of the cyclic alkylene carbonate with water. Therefore, it is especially attractive to separate carbon dioxide and recycle the carbon dioxide thus obtained to step (a) either as such or after having been purified. The extent to which the carbon dioxide is purified depends on the nature and the amounts of contaminants present in the carbon dioxide. These again depend on the exact reaction conditions and purification steps of the process.

The alkylene oxide is reacted with carbon dioxide at operating conditions which are well known to be suitable.

Such process conditions will generally comprise a temperature of from 50 to 200 °C, more specifically of from 100 to 150 °C. The pressure generally will be at least  $5 \times 10^5$  N/m<sup>2</sup>, more specifically the pressure will generally be of from 5 to  $100 \times 10^5$  N/m<sup>2</sup>, preferably of from 8 to  $50 \times 10^5$  N/m<sup>2</sup>, more preferably of from 10 to  $30 \times 10^5$  N/m<sup>2</sup>.

The catalyst can be added to the reactor in any form known to be suitable to someone skilled in the art. Generally, the catalyst will be added as such or as a solution of the catalyst preferably in a solvent such as a cyclic carbonate or alkylene glycol. The catalyst can be added either to the alkylene oxide or to the carbon dioxide or to the mixture of both. Preferably, the catalyst solution is added to the reactor containing the mixture of alkylene oxide and carbon dioxide.

The reaction mixture obtained in step (a) can be used without further purification in the manufacture of alkylene glycol. However, some purification of the reaction mixture can be carried out. A purification which can be advantageous is the removal of at least part of the carbon dioxide from the reaction mixture obtained in step (a) before subjecting the remainder of the reaction mixture to step (b). Such purification can substantially reduce the volume of the reaction mixture to be subjected to step (b).

The first reaction mixture to be subjected to step (b) and referred to in the present invention, can be either the first reaction mixture obtained in step (a) which has not been treated further, or the first reaction mixture of step (a) which has been treated further in step (b), or a mixture of both the product of step (a) and the product of step (b). As mentioned hereinbefore,

it is preferred that at least part of the first reaction mixture is subjected to step (b) before sending it to step (b).

5 Process step (a) is preferably carried out with the help of a homogeneous catalyst while step (b) is carried out with the help of a heterogeneous catalyst. It has been found to be especially advantageous if the homogeneous catalyst for process step (a) is present in step (b). Without wishing to be bound to any theory, it is thought that the presence of the catalyst for process  
10 step (a) reduces the amount of by-products formed in the conversion of alkylene oxide to alkylene glycol in step (b). Removal of a limited amount of the homogeneous catalyst can occur during distillation or further processing of reaction mixture. However, such processes  
15 generally will leave sufficient homogeneous catalyst in the reaction mixture to serve its purpose in step (b) of the present process. A further improvement was observed if the homogeneous catalyst was present in combination with a substantial amount of carbon dioxide. Therefore,  
20 it is preferred in the present process to send the first reaction mixture directly from step (a) to step (b) while removing at most part of the carbon dioxide still present. It was found that such set-up gave less by-products such as dipropylene glycol.  
25

The homogeneous catalyst which is preferably present in the crude reaction product of step (b), can be separated off from the second reaction mixture and recycled for use in step (a). The catalyst can be  
30 recycled in combination with further compounds either added to or formed in the process according to the present invention. Usually, the catalyst will be recycled

while being dissolved in unconverted cyclic alkylene carbonate.

5 A substantial amount of alkylene oxide is present in step (b). Preferably, the amount of alkylene oxide and cyclic carbonate which is present in step (b) is such that the molar ratio of alkylene oxide to cyclic carbonate is of from 0.01 mole of alkylene oxide per mole of cyclic carbonate to 1 mole of alkylene oxide per mole of cyclic carbonate, i.e. of from 0.01:1 to 1:1, more preferably of from 0.02:1 to 0.6:1, more preferably of from 0.03:1 to 0.4:1, more preferably of from 0.04:1 to 0.3:1, more preferably of from 0.05:1 to 0.2:1. Most preferably, the molar ratio of alkylene oxide to cyclic carbonate is of from 0.08:1 to 0.15:1.

15 The first reaction mixture obtained in step (a) can contain the desired amount of alkylene oxide due to the fact that part of the alkylene oxide has not been converted in step (a) and/or alkylene oxide can be added in step (b).

20 In a preferred embodiment, part of the alkylene oxide which is present in step (a) is not converted in step (a) and is present in the feed of step (b). The exact amount of alkylene oxide which is not converted, can vary widely as further alkylene oxide can be added in process step (b). If no further alkylene oxide is added in step (b), it is preferred that of from 60 to 99% of the alkylene oxide present in the feed of step (a) is converted in step (a). More specifically, of from 60 to 95% of the alkylene oxide present in the feed of step (a) is converted in step (a) in this embodiment, most specifically of from 70 to 90 %wt. This preferred embodiment has the advantage over a conventional set-up that the reactor for step (a) can be smaller than for a

conventional process as the complete conversion of alkylene oxide does not need to be ensured while the capacity can be reduced of both the cooling equipment for step (a) and the heating equipment for step (b).

5       The most preferred embodiment of the present invention comprises converting the alkylene oxide present in the feed of step (a) substantially fully in step (a), and adding additional alkylene oxide in step (b). The substantially full conversion in step (a) means that the majority of the alkylene oxide is converted in step (a),  
10       more specifically at least 80% of the alkylene oxide is converted. The addition of additional alkylene oxide can be carried out before and/or during step (b). This set-up has the advantage that the alkylene oxide can be added  
15       during step (b) such that an optimum temperature profile is attained over the reactor for step (b). In such case, it will usually be preferred to add the additional alkylene oxide partly to the first reaction mixture before step (b) and partly during the conversion of the  
20       first reaction mixture in step (b). In a further preferred embodiment, the alkylene oxide added to step (b) is added at different stages of conversion of step (b). Such addition makes that optimum use is made of the heat generated by the hydrolysis of alkylene oxide in  
25       step (b).

      In step (b) of the present invention, the cyclic carbonate is contacted with water. The heterogeneous catalysts for use in such process, are well known in the art. Examples of such catalysts comprise solid inorganic  
30       compounds such as alumina, silica-alumina, silica-magnesia, aluminosilicate, gallium silicate, zeolites, metal-exchanged zeolites, ammonium-exchanged zeolites, zinc on a support, lanthanum on a support, a mixture of

aluminium and magnesium (hydr)oxide and ion-exchange resins.

Preferably, the heterogeneous catalyst employed in step (b) is chosen from the group consisting of a mixture of aluminium and magnesium (hydr)oxide, zinc on a support, lanthanum on a support and alumina. These catalysts will be described hereinafter in more detail.

The mixture of aluminium and magnesium (hydr)oxide preferably has a magnesium to aluminium molar ratio in the range of from 3 to 50, more preferably of from 4 to 20. In the preparation of the catalyst, generally a so-called mixed magnesium/aluminium hydroxide is formed. However, it might be that under working conditions mixed magnesium/aluminium oxides are present. Our reference to a mixture of aluminium and magnesium (hydr)oxide covers both mixtures of aluminium and magnesium hydroxide and mixtures of aluminium and magnesium oxide and a combination of both mixtures. These mixtures were found to give the highest activity at a molar ratio of more than 3, preferably more than 4. A preferred range was found to be of from 4 to 20, more specifically of from 5 to 15, most specifically of from 5 to 10. Preferred catalysts are described in International application No. PCT/EP02/12640 (our TS 1067).

In another preferred embodiment of the present invention, the catalyst comprises a lanthanum compound on a support. A preferred catalyst comprises at least 7 %wt of lanthanum supported on a support. The lanthanum compound preferably is  $\text{La}_2\text{O}_3$  or a precursor thereof.

Under reaction conditions this lanthanum compound may be temporarily and/or reversibly converted due to the reaction conditions into lanthanum hydroxide ( $\text{La}(\text{OH})_3$ ),

lanthanumoxyhydroxide ( $\text{LaO}(\text{OH})$ ) and/or corresponding alcoholate species such as ( $\text{La}(\text{OR})_3$  or  $\text{LaO}(\text{OR})$ ).

As a support for the lanthanum containing catalyst any suitable support may be used. The support preferably is substantially inert under the reaction conditions and is provided with sufficient mechanical strength.

Potential supports comprise clay minerals, inorganic supports such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{ZnO}$  and mixtures thereof. Other examples are a kaolinite, a hallosyte, a chrysotile, a montmorillonite, a beidellite, a hectorite, a sauconite, a muscovite, a phlogopite, a biotite, a hydrotalcite and talc. Particularly preferred are the inorganic supports selected from the group consisting of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{ZnO}$  and mixtures thereof.

The lanthanum containing catalyst preferably comprises at least 7 %wt of lanthanum, more specifically in the range of from 7 to 40 %wt of lanthanum based on total amount of catalyst. The lanthanum containing catalyst may be produced using any suitable method. A preferred method comprises impregnating a support with a lanthanum containing salt, and subsequently drying and calcining the impregnated support. After impregnation the impregnated support can be dried and subsequently calcined. Calcination is generally carried out at a calcination temperature from between 120 to 700 °C. The catalyst activity can be increased even further if the catalyst is calcined at a temperature in the range of from 350 to 600 °C. Preferred catalysts are described in PCT patent application No. PCT/EP02/12638 (our TS 1144).

A further catalyst which is especially suitable for use in step (b) of the present invention is a zinc supported catalyst. The support preferably is selected

from the group consisting of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Cr}_2\text{O}_3$ , carbon and mixtures thereof. The zinc supported catalyst can be prepared by impregnation of silica, alumina or mixtures of aluminium and magnesium (hydr)oxide with a zinc nitrate solution. Preferably, the zinc supported catalysts comprise at least 15 %wt of zinc on a support having a surface area of at least  $20 \text{ m}^2/\text{g}$ , more preferably at least  $40 \text{ m}^2/\text{g}$ . Preferred catalysts are described in the patent applications claiming priority of European patent application No. 02256347.2 (our TS 1199, not yet published).

A further catalyst which is preferably used is a catalyst consisting of alumina. Preferably, the alumina is gamma-alumina.

The hydrolysis of process step (b) is preferably carried out at a temperature of from  $50$  to  $300^\circ\text{C}$ , preferably of from  $80$  to  $250^\circ\text{C}$ , more specifically of from  $100$  to  $200^\circ\text{C}$ . The pressure can vary widely, and preferably is at most  $100 \times 10^5 \text{ N/m}^2$ , more specifically at most  $60 \times 10^5 \text{ N/m}^2$ , more specifically at most  $40 \times 10^5 \text{ N/m}^2$ . The pressure will usually be at least  $1 \times 10^5 \text{ N/m}^2$ , more specifically at least  $5 \times 10^5 \text{ N/m}^2$ .

Preferably, alkylene glycol is separated from the second reaction mixture. The alkylene glycol can be separated from the reaction mixture obtained in step (b) in any way known in the art. A preferred separation comprises distillation of the second reaction mixture, optionally followed by further distillation of one or more of the distillate fractions and/or bottom fractions. One or more of the fractions separated will have a high content of alkylene glycol. Alkylene glycol obtained by distillation will usually be sufficiently pure to use as



such. If required, small amounts of by-products can be removed separately.

The present invention is further illustrated by the following example. The example is given for further illustration of the invention and is not limiting the invention.

#### Examples

A 1 litre high-pressure autoclave reactor was loaded with 0.5 gram of MgO catalyst, to which were added propylene carbonate (PC), water, propylene oxide (PO) and 1,2-propanediol (monopropylene glycol, MPG). The amounts of the compounds (in mmole) are shown in Table 1. In Example 1, 0.5 gram of methyltributylphosphonium iodide catalyst (MTBPI) was added as well. The reactor was purged with N<sub>2</sub> or CO<sub>2</sub> and subsequently the autoclave was heated to 150 °C during the indicated number of hours. In some experiments, the reactor is additionally pressurized with CO<sub>2</sub>.

At the end of the run, the autoclave was cooled to room temperature and the liquid was removed for off-line analysis by gas chromatography with the help of sulfolane as the standard. The amounts of the compounds in the product (in mmole) are shown in Table 1. A well-known by-product is dipropylene glycol (DPG). A limited amount of further by-products was present in the product. The further by-products have not been analysed. The results are shown in Table 1.

It is clear from Table 1 that propylene oxide present in the feed is converted while only a limited amount of dipropylene glycol is formed. Further reduction of the formation of dipropylene glycol is observed if the homogeneous catalyst for the conversion of alkylene oxide

into cyclic carbonate is present during the hydrolysis of the cyclic carbonate.

Table 1

	time (h)	catalyst	feed						product			
			PC	MPG	H <sub>2</sub> O	PO	CO <sub>2</sub> (bar)	PC	MPG	PO	DPG	
1	14	MgO/MTBPI	500	120	720	100	22	160	490	1	0	
2	13	MgO	500	60	730	100	22	230	330	1	6	
3	13	MgO	500	110	660	50	-	200	410	1	2	
4	5	MgO	500	100	600	100	-	350	260	53	3	
5	5	MgO	500	120	670	50	-	310	240	9	1	



C L A I M S

1. Process for the preparation of alkylene glycol from alkylene oxide, which process comprises:

(a) contacting alkylene oxide with carbon dioxide in the presence of catalyst to obtain a first reaction mixture containing cyclic carbonate, and

(b) contacting at least part of the first reaction mixture with water in the presence of catalyst to obtain a second reaction mixture containing alkylene glycol and carbon dioxide,

in which process a substantial amount of alkylene oxide is present in step (b).

2. Process according to claim 1, in which process the molar ratio of alkylene oxide to cyclic carbonate in step (b) is of from 0.01:1 to 1:1.

3. Process according to claim 1 and/or 2, in which process step (a) is carried out with the help of a homogeneous catalyst and step (b) is carried out with the help of a heterogeneous catalyst.

4. Process according to claim 3, in which process homogeneous catalyst for process step (a) is present in step (b).

5. Process according to any one of the preceding claims, in which process the alkylene oxide present in the feed of step (a) is substantially fully converted, and which process further comprises adding additional alkylene oxide in step (b).

6. Process according to any one of claims 1 to 4, in which process of from 60 to 99% of the alkylene oxide present in the feed of step (a) is converted in step (a).

7. Process according to any one of claims 1 to 6, in which process alkylene glycol is separated from the second reaction mixture.

A B S T R A C T

PROCESS FOR THE PREPARATION OF ALKYLENE GLYCOL

Process for the preparation of alkylene glycol from alkylene oxide, which process comprises:

(a) contacting alkylene oxide with carbon dioxide in the presence of catalyst to obtain a first reaction mixture containing cyclic carbonate, and

(b) contacting at least part of the first reaction mixture with water in the presence of catalyst to obtain a second reaction mixture containing alkylene glycol and carbon dioxide,

in which process a substantial amount of alkylene oxide is present in step (b).

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